

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-123084

(43)Date of publication of application : 15.05.1998

(51)Int.Cl.

G01N 27/12

(21)Application number : 09-114152

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(22)Date of filing : 27.03.1997

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(30)Priority

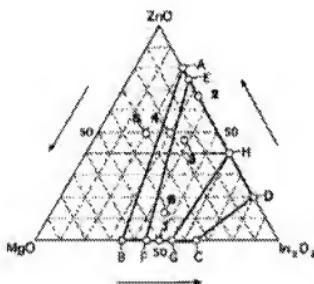
Priority number : 08244292 Priority date : 26.08.1996 Priority country : JP

## (54) SEMICONDUCTOR GAS SENSOR

### (57)Abstract:

PROBLEM TO BE SOLVED: To provide a semiconductor gas sensor which is simple in structure, can be manufactured safely, inexpensively and easily, and has high sensitivity and superior gas selectivity to chlorine, fluorine and ozone gas.

SOLUTION: The sensor is formed of a composite metallic oxide primarily composed of magnesium(Mg), zinc(Zn) or indium(In), or indium oxide of Mg and In or Zn and In. The oxide is a composite metallic oxide of  $MgO-In_2O_3$ ,  $ZnO-In_2O_3$  or  $MgO-ZnO-In_2O_3$ , which is formed by adding a small amount of a composite oxide including at least one kind of  $In_2O_3$  components whose composition lies in a composition area ABCD or at least one element other than the composing elements.



## CLAIMS

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[Claim(s)]

[Claim 1]Magnesium (Mg), zinc (Zn) and indium (In), or Zn and In, Or a semiconductor gas sensor by which a remarkable resistance increment being shown to chlorine, fluoride, and gaseous ozone using a composite metal oxide which uses as a base indium oxide which comprises Mg and In.

[Claim 2]A semiconductor gas sensor, wherein the composite metal oxide according to claim 1 shows a remarkable resistance increment to chlorine, fluoride, and gaseous ozone which comprise a  $MgO-In_2O_3$  system, a  $ZnO-In_2O_3$  system, or a  $MgO-ZnO-In_2O_3$  system.

[Claim 3]A semiconductor gas sensor, wherein the  $MgO-ZnO-In_2O_3$  system composite metal oxide according to claim 2 shows a remarkable resistance increment to chlorine and fluorine gas which comprise the presentation field ABCD and component composition preferably surrounded by EFGH in [drawing 1].

[Claim 4]A semiconductor gas sensor, wherein the  $MgO-ZnO-In_2O_3$  system composite metal oxide according to claim 2 shows a remarkable resistance increment to gaseous ozone which comprises the presentation field ABCD and component composition preferably surrounded by EFGH in [drawing 1].

[Claim 5]A semiconductor gas sensor, wherein a composite metal oxide Claims 1, 2 and 3 or given in four shows a remarkable resistance increment to this oxide to at least one or more sorts of chlorine, fluoride, and gaseous ozone other than a constituent element which add a little arbitrary elements.

[Claim 6]A semiconductor gas sensor, wherein a composite metal oxide Claims 1, 2, 3 and 4 or given in five shows a remarkable resistance increment to chlorine, fluoride, and gaseous ozone which comprise an amorphous substance.

[Claim 7]In manufacture and a synthetic process of various chemicals as this object for gas detection or an object for Measurement Division for protecting various buildings, industrial machinery, industrial material, or a living thing from damage caused by harmful chlorine and fluorine gas, The semiconductor gas sensor according to claim 1, 2, 3, 5, or 6 used in order to manufacture an object for detection or a gas sensor for Measurement Division of this gas produced mainly or secondarily.

[Claim 8]As an object for detection or an object for Measurement Division of gaseous ozone mainly used in sterilization, hygiene supervision, etc. in manufacture and a synthetic process, and a water-and-sewage institution of various chemicals and drugs, and foodstuffs, Or the semiconductor gas sensor according to claim 1, 2, 4, 5, or 6 used as an object for the surveillance monitors of an ozone layer in the atmosphere which is effective in protecting all the living things which live on the earth from harmful ultraviolet rays.

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[Translation done.]

## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to a gas sensor.

[0002]

[The conventional method] Now, the method using ultraviolet absorption, chemiluminescence, and a chemical reaction is mainly used for detection of chlorine and

fluorine gas. The method using infrared absorption spectroscopy or a chemical reaction is mainly used for detection of gaseous ozone.

[0003]

[Problem(s) to be Solved by the Invention] Since structure is complicated and large-sized, and very expensive compared with the semiconductor gas sensor which used for the main raw material now the metallic oxides (for example, tin oxide etc.) used for the propane detector for home use etc., this kind of gas sensor has not come [ however, ] to spread broadly. On the other hand, in a semiconductor gas sensor, although it is known that there is detection sensitivity mainly to combustible gas, the gas sensor which shows practical detection sensitivity to chlorine and fluorine gas, and has the outstanding gas selectivity is not realized. Therefore, as this object for gas detection or the object for Measurement Division for protecting various buildings, industrial machinery, industrial material, or a living thing from the damage caused by harmful chlorine and fluorine gas, Or it is anxious for realization of chlorine with sensitivity inexpensive as the object for detection or the object for Measurement Division of this gas produced mainly or secondarily in manufacture and the synthetic process of various chemicals, and high, and the outstanding gas selectivity, and a fluoride gas sensor. The semiconductor gas sensor which shows practical detection sensitivity to gaseous ozone, and has the outstanding gas selectivity on the other hand is not realized, either. Therefore, as the object for detection or the object for Measurement Division of this gas mainly used in the sterilization, hygiene supervision, etc. in manufacture and synthetic process, and water-and-sewage institution of various chemicals and drugs, and foodstuffs, or it is anxious for realization of the gaseous ozone sensor with sensitivity inexpensive as an object for the surveillance monitors of the ozone layer in the atmosphere which is effective in protecting all the living things which live on the earth from harmful ultraviolet rays, and high, and the outstanding gas selectivity. This invention is simple for structure, and it can manufacture safely, inexpensive, and easily, and aims at providing the semiconductor gas sensor in which high sensitivity and the outstanding gas selectivity are shown to chlorine, fluoride, and gaseous ozone.

[0004]

[Means for Solving the Problem] A semiconductor gas sensor which grows into this invention Magnesium (Mg), zinc (Zn), and indium (In), Or a composite metal oxide which uses as a base indium oxide which comprises Mg and In, or Zn and In, With namely, a MgO-ZnO-In<sub>2</sub>O<sub>3</sub> system composite metal oxide in which this oxide contained a MgO-In<sub>2</sub>O<sub>3</sub> system and a ZnO-In<sub>2</sub>O<sub>3</sub> system. It can attain by constituting from this oxide that adds at least one sort of elements [ a little ] other than composite metal oxides which use as a base indium oxide surrounded in the presentation field ABCD shown by [drawing 1], or these constituent elements. Gallium (Ga), aluminum (aluminum), tin (Sn), platinum (Pt), especially palladium (Pd), etc. were effective as this small-quantity additive. Although it can use in arbitrary form, such as a thin film, a thick film, and a sintered compact, and can use with arbitrary material forms, such as a single crystal, polycrystal, or an amorphous substance, this oxide is preferably more nearly amorphous than a crystalline substance, and is used. A composite metal oxide which constitutes a semiconductor gas sensor which grows into this invention is realizable with a publicly known synthetic method and a manufacturing method.

[Drawing 1]

[0005]

[Function] As for the semiconductor gas sensor which grows into this invention, electrical resistance increases remarkably to contact of chlorine, fluoride, and gaseous ozone. On the other hand, to organic volatile gas, such as combustible gas, such as other gas, for example,

hydrogen, methane, hexane, butane, or propane, or acetone, and alcohol, reduction in resistance is shown conversely. It has the feature that the presentations of this composite metal oxide in which increase of the most remarkable electrical resistance is shown to contact of chlorine, fluoride, and gaseous ozone differ, respectively. Therefore, it this gas sensor that grows into this invention not only has the identifiable extremely outstanding gas selectivity for the kind of gas by the change in the resistance of a sensor, but has the feature that the gas selectivity of a sensor is controllable, by controlling the presentation of this composite metal oxide. . The group II element which was adopted with this gas sensor that grows into this invention and which used indium oxide as the base is included. For example, it has the conductivity by the free electron considered that  $MgO-In_2O_3$ ,  $ZnO-In_2O_3$ , or a  $MgO-ZnO-In_2O_3$  system composite metal oxide originates in an intrinsic lattice defect. The oxygen gas in the atmosphere sticks to this oxide surface heated by about 200-400 \*\* in the air, it functions as an electron trap, and resistance of this oxide is made to increase. If this oxide surface of such a state is put to chlorine, fluoride, or gaseous ozone, In order for the atomic oxygen which has the very strong oxidation generated when chlorine, fluoride, or ozone decomposes to adsorb violently, to function as an electron trap and to decrease the free electron density in this oxide, the remarkable operation effect of high-resistance-izing remarkably was accepted. On the other hand, in the case where it is put to combustible gas, in order to make the oxygen which stuck to this oxide surface by the reducing action of this gas desorb, resistance decreases. Chlorine or the fluoride which stuck to this oxide surface, It combines with the moisture in the air, etc. and desorbs in the form of  $HCl$  or  $HF$  gas, respectively, and it combines with the moisture in the air, etc. and the atomic oxygen to which it stuck is desorbed in the form of  $H_2O$ , and when the function as an electron trap falls, it returns to an initial state. However, if the atomic oxygen generated when chlorine, fluoride, or gaseous ozone decomposes again adsorbs, the function as an electron trap will increase and an above-mentioned process will be repeated. Adding at least one sort of elements, for example, aluminum,  $Ga(s)$ ,  $Sn$ ,  $Pt(s)$ , or  $Pd$  other than a constituent element, etc. to this oxide, It contributes to promotion of the decomposition reaction in the surface or the activation on the surface of a grain boundary, and amorphous-ization, and, in addition to those effects, chlorine or atomic oxygen is considered that an adsorbing function becomes remarkable for an operation of surface-activity-izing. These operation effects mentioned above receive chlorine and fluorine gas, Also in this composite metal oxide that has the presentation field ABCD and the ingredient preferably surrounded by EFGH of [drawing 1]. Especially, As opposed to  $MgO-In_2O_3$  whose quantity of 2  $ZnO-In_2O_3$  which is a  $ZnO-In_2O_3$  system presentation is a  $MgO-In_2O_3$  system presentation. 30-85 -- desirable -- 40-80-mol% -- it was remarkable in this composite metal oxide to contain. On the other hand to gaseous ozone, especially, as opposed to 2  $ZnO-In_2O_3$  whose  $MgO-In_2O_3$  which is a  $MgO-In_2O_3$  system presentation is a  $ZnO-In_2O_3$  system presentation -- 70-95 -- desirable -- 80-90-mol% -- it was remarkable in this composite metal oxide to contain, namely, the range ABCD of the metallic element composition ratio of this composite metal oxide corresponding to an above-mentioned presentation -- the operation effect was preferably remarkable at EFGH. An embodiment explains this invention below.

[0006]

[Work example 1]Using  $MgO$  and  $In_2O_3$  as a raw material, both powder is mixed so that about 50-mol% of  $MgO$  may be contained to 203 atoms of  $In(s)$ , It is calcinated at 1000 \*\* among an argon (Ar) gas atmosphere, and the indium oxide magnesium ( $MgO-In_2O_3$ ) powder shown in the presentation 1 of [drawing 1] is manufactured. Next, using  $ZnO$  and  $In_2O_3$  as a raw material, both powder is mixed so that about 66.7-mol% of  $ZnO$  may be

contained to  $\text{In}_2\text{O}_3$ , The indium oxide zinc ( $2\text{ZnO}\text{-}\text{In}_2\text{O}_3$ ) powder which calcinates it at 1000 \*\* among Ar gas atmosphere, and is shown in the presentation 2 of [the figure] is produced.  $2\text{ZnO}\text{-}\text{In}_2\text{O}_3$  powder is received using this  $\text{MgO}\text{-}\text{In}_2\text{O}_3$  powder and this  $2\text{ZnO}\text{-}\text{In}_2\text{O}_3$  powder,  $\text{MgO}\text{-}\text{In}_2\text{O}_3$  powder -- 40-mol% -- the mixed powder mixture at 1000 \*\* among Ar gas atmosphere. [ calcinate and ] Using the indium oxide magnesium zinc ( $2\text{MgO}$ ,  $6\text{ZnO}$ , and  $5\text{In}_2\text{O}_3$ ) powder or sintered compact shown in the presentation 3 of manufactured [the figure] as a target with high frequency magnetron sputtering equipment. Composite metal oxide thin film  $2\text{MgO}$ ,  $6\text{ZnO}$ , and  $5\text{In}_2\text{O}_3$  were formed on the glass substrate. It was checked by electron probe microanalyzer (EPMA) that the metallic element composition ratio of this thin film is almost the same as that of this target. X diffraction measurement showed that this film was amorphous. The resistivity of this oxide film was a low value called  $4 \times 10^{-4}$  omegacm. The gold electrode was formed in the surface of this film by the sputtering method, and the gas sensor was manufactured. When this gas sensor operated at 300 \*\* among the air was put to about 350 ppm methane and 80 ppm gaseous chlorine, this gas sensor showed resistance reduction to methane, and showed very big resistance increase to gaseous chlorine. Each sensitivity was- [ +80% (+ shows resistance reduction) of ] 11000% (- shows a resistance increment). Those results are shown in [Table 1]. The sensor which comprises the further above-mentioned  $\text{MgO}\text{-}\text{In}_2\text{O}_3$  (presentation 1 of [drawing 1]) composite-metal-oxide thin film, The same tendency was accepted also in the sensor which comprises a  $2\text{ZnO}\text{-}\text{In}_2\text{O}_3$  (presentation 2 of [drawing 1]) composite metal oxide thin film, and sensitivity was- [-120% of ] 130% respectively in the case where gaseous chlorine is received. These results show that the gas sensor concerning this invention has very high sensitivity and the outstanding gas selectivity to gaseous chlorine. The response characteristic over gaseous chlorine (the concentration 50 and 1, 0.5, 0.2 ppm) is shown in [drawing 2]. The figure shows that have very high sensitivity and this sensor shows a quick response to gaseous chlorine. The gaseous chlorine concentration dependence of the sensor element sensitivity to gaseous chlorine is shown in [drawing 3]. In the range of about 0.1-50 ppm of levels of chlorine, sensitivity rose with the increase in gaseous chlorine concentration. Here, sensitivity set the resistance after contacting the resistance of the sensor before making gas contact in  $\text{R}_0$  and gas to  $\text{R}$ , and asked for the sensitivity  $S$  to each gas as  $1 (\text{R}_0\text{-}\text{R}) / \text{S} = \{\text{R}_0\} \times 100\%$ . Here, the sensitivity  $S$  in case the value of  $\text{R}$  increases to  $\text{R}_0$  wrote negative and it in the case of decreasing as positive. On the other hand, when this gas sensor was put to fluorine gas, the almost same gas sensitive detector characteristic as the case where it puts to gaseous chlorine was obtained.

表1

メタン	塩素
$2\text{MgO}\text{-}6\text{ZnO}\text{-}5\text{In}_2\text{O}_3$	+ 80% - 11000%

[Drawing 2]

[Drawing 3]

[0007]

[Work example 2]  $\text{MgO}$ ,  $\text{ZnO}$ , and  $\text{In}_2\text{O}_3$  -- respectively -- 20, 50, and 30-mol% -- it mixing uniformly and so that it may contain, The indium oxide magnesium zinc ( $2\text{MgO}$ ,  $5\text{ZnO}$ , and  $3\text{In}_2\text{O}_3$ ) powder which calcinates them at 1000 \*\* among a argon (Ar) gas atmosphere, and is shown with the presentation 4 of [drawing 1] is produced. Next,  $2\text{MgO}$ ,  $5\text{ZnO}$ , and a

$3\text{In}_2\text{O}_3$  composite metal oxide film were formed on the glass substrate with high frequency magnetron sputtering equipment, using this powder as a target. It was checked by EPMA that the metal composition ratio of this film is almost the same as this target metal composition ratio. The resistivity of this oxide film was a low value called abbreviation  $9 \times 10^{-4}$  omegacm. The gold electrode was formed in the surface of this film by the sputtering method, and the gas sensor was produced. The sensitivity to methane and gaseous chlorine when contacting about 350 ppm methane and 80 ppm gaseous chlorine in this sensor operated at 300 \*\* is shown in [Table 2] among the air. To contact of gas, this sensor showed resistance reduction to methane, and showed big resistance increase to gaseous chlorine. These results show that the gas sensor which grows into this invention has high sensitivity and the outstanding gas selectivity to gaseous chlorine like said embodiment. On the other hand, when this gas sensor was put to fluorine gas, the almost same gas sensitive detector characteristic as the case where it puts to gaseous chlorine was obtained.

表2

	メタン	塩素
$2\text{MgO} \cdot 5\text{ZnO} \cdot 3\text{In}_2\text{O}_3$	80%	-900%

[0008]

[Work example 3]  $\text{MgO}$ ,  $\text{ZnO}$ , and  $\text{In}_2\text{O}_3$  -- respectively -- 30, 50, and 20-mol% -- it mixing uniformly and so that it may contain. The magnesium oxide indium zinc ( $3\text{MgO}$ ,  $5\text{ZnO}$ , and  $2\text{In}_2\text{O}_3$ ) powder which calcinates at 1000 \*\* among Ar gas atmosphere, and is shown with the presentation 5 of [drawing 1] was produced.  $3\text{MgO}$ ,  $5\text{ZnO}$ , and a  $2\text{In}_2\text{O}_3$  composite metal oxide film were formed on the glass substrate with high frequency magnetron sputtering equipment, using this powder as a target. It was checked by EPMA that the metal composition ratio of this film is almost the same as that [ metal composition ] of this target. The resistivity of this composite metal oxide film was a  $2 \times 10^{-3}$  omegacm grade. The place which this element was operated at about 300 \*\* among the air, and was put to about 300 ppm various gas to be examined. It turned out that this sensor shows remarkable resistance increase to gaseous chlorine, and presents resistance reduction to combustible gas, such as other gas, for example, hydrogen, methane, butane, and methanol, and it has the outstanding gas selectivity as shown in [Table 3]. On the other hand, when this gas sensor was put to fluorine gas, the almost same gas sensitive detector characteristic as the case where it puts to gaseous chlorine was obtained.

表3

	水素	メタン	ブタン
$3\text{MgO} \cdot 5\text{ZnO} \cdot 2\text{In}_2\text{O}_3$	+ 8.0 %	+ 7.5 %	+ 1.7 %
<hr/>			
塩素	メタノール		
<hr/>			
- 13.0 %	3.0 %		
<hr/>			

## [0009]

[Work example 4]Indium oxide magnesium zinc ( $2\text{MgO}$ ,  $6\text{ZnO}$ , and  $5\text{In}_2\text{O}_3$ ) powder of the same presentation as the presentation 3 of [drawing 1] mentioned above is targeted, A sensor element which comprises  $2\text{MgO}$ ,  $6\text{ZnO}$ , and a  $5\text{In}_2\text{O}_3$  amorphous composite metal oxide film produced using the laser ablation method was produced. Resistivity of this oxide film was a  $5.5 \times 10^{-4}$  omega cm grade. A place put to combustible gas which this element was operated at about 350 \*\* among the air, and was described in about 80 ppm gaseous chlorine and about 300 ppm Embodiment 3, This sensor presented a sensitivity characteristic that remarkable resistance increase was shown to gaseous chlorine, and resistance reduction was shown to other gas, and having said high sensitivity and similarly outstanding gas selectivity became whether to be \*\*. Sensitivity to chlorine was -1900%. Sensitivity to other combustible gas was the same as that of said Embodiment 3 almost, and the gas sensitive detector characteristic to fluorine gas was the same as that of a case of gaseous chlorine almost.

## [0010]

[Work example 5] $\text{MgO}$ ,  $\text{ZnO}$ , and  $\text{In}_2\text{O}_3$  -- respectively -- 20, 50, and 30-mol% -- the compound metal oxide powder which comprises the magnesium oxide indium zinc which is uniformly mixed so that it may contain, calcinates at 1000 \*\* among Ar gas atmosphere, and is shown with the presentation 4 of [drawing 1] was produced. A polyvinyl butyral (PVB), a polyethylene glycol (PEG), toluene, and ethanol were added by the ratio of 9:4:52:35 to this powder, it mixed to it, and the after-grinding slurry was produced. The ceramic sensor sintered in the size of  $2\text{x}5\text{x}10\text{ mm}$  of outsides using this was produced. The resistivity of these ceramics was a  $2 \times 10^{-3}$  omega cm grade. The place which carried out heating maintenance of this element among the air at about 275 \*\*, and was put to about 300 ppm gaseous chlorine, It turned out that said same result that this sensor shows the remarkable resistance increment of -1020% to gaseous chlorine, and resistance reduction is shown to other gas, for example, combustible gas, is obtained, and has the outstanding gas selectivity. In the sensor which added and produced about 2.0% of  $\text{Ga(s)}$  [ a little ] to this composite metal oxide, the sensitivity to chlorine reached the above-mentioned twice [ about ]. Even when aluminum, Sn, Pt, or Pd was added as an alloying element, the almost same result as the case of  $\text{Ga}$  was obtained. The gas sensitive detector characteristic to fluorine gas was the same as that of the case of gaseous chlorine almost.

## [0011]

[Work example 6]Using  $\text{MgO}$  and  $\text{In}_2\text{O}_3$  as a raw material, both powder is mixed so that about 50-mol% of  $\text{MgO}$  may be contained to  $2\text{O}_3$  atoms of  $\text{In(s)}$ , It is calcinated at 1000 \*\*

among an argon (Ar) gas atmosphere, and indium oxide magnesium ( $MgO-In_2O_3$ ) powder shown in the presentation 6 of [drawing 1] is manufactured. Next, using  $ZnO$  and  $In_2O_3$  as a raw material, both powder is mixed so that about 66.7-mol% of  $ZnO$  may be contained to  $In_2O_3$ , Indium oxide zinc ( $2ZnO-In_2O_3$ ) powder which calcinates it at 1000 \*\* among Ar gas atmosphere, and is shown in the presentation 2 of [the figure] is produced. This  $MgO-In_2O_3$  powder and this  $2ZnO-In_2O_3$  powder are used, as opposed to  $2ZnO-In_2O_3$  powder --  $MgO-In_2O_3$  powder -- 80-mol% -- mixed powder mixture at 1000 \*\* among Ar gas atmosphere. [ calcinate and ] Using indium oxide magnesium zinc ( $4MgO$ ,  $2ZnO$ , and  $5In_2O_3$ ) powder or a sintered compact shown in the presentation 6 of manufactured [the figure] as a target with high frequency magnetron sputtering equipment. Composite metal oxide thin film  $4MgO$ ,  $2ZnO$ , and  $5In_2O_3$  were formed on a glass substrate. It was checked by electron probe microanalyzer (EPMA) that metallic element composition ratio of this thin film is almost the same as that of this target. X diffraction measurement showed that this film was amorphous. Resistivity of this oxide film was a low value called  $9 \times 10^{-4}$  omegacm. A gold electrode was formed in the surface of this film by a sputtering method, and a gas sensor was manufactured. When this sensor operated at 275 \*\* among the air was put to about 1 ppm of gaseous ozone, this sensor showed very big resistance increase, and the sensitivity was abbreviation-300%. Those results are shown in [Table 1]. Sensitivity was -200%, when same tendency was accepted also in a sensor which comprises the further above-mentioned  $MgO-In_2O_3$  (presentation 1 of [drawing 1]) composite metal oxide thin film and it put to gaseous ozone which is about 1 ppm. These results show that a gas sensor concerning this invention has very high sensitivity and the outstanding gas selectivity to gaseous ozone. [drawing 4] -- \*\*\*\* -- the gaseous ozone concentration dependence of sensor element sensitivity to gaseous ozone is shown. In the range with a gaseous ozone concentration of about 0.5-5 ppm, sensitivity rose with an increase in gaseous chlorine concentration.

表4

オゾン

$4MgO \cdot 2ZnO \cdot 5In_2O_3$  - 300%

[Drawing 4]

[0012]This invention is not limited to the above-mentioned embodiment. As mentioned above, even if it uses various kinds of publicly known synthetic methods and manufacturing methods, the almost same result is obtained.

[Effect of the Invention]Since this gas sensor that grows into this invention can produce the oxide containing zinc, magnesium, and indium as a main raw material, handling has safety and the feature that it is easy and structure can manufacture simply inexpensive moreover. This gas sensor by this invention has the outstanding gas selectivity which is not in the former that a very big resistance increment is shown to chlorine, fluoride, and gaseous ozone, and resistance reduction is conversely shown to other gas by controlling a presentation. As this object for gas detection or the object for Measurement Division for protecting various buildings, industrial machinery, industrial material, or a living thing from the damage caused by harmful chlorine and fluorine gas by using this gas sensor. Or as the chlorine which has an effect prominent as the object for detection or the object for Measurement Division of this gas produced mainly or secondarily in manufacture and the synthetic process of various chemicals, and a fluoride gas sensor, As the object for detection or the object for

Measurement Division of the gaseous ozone mainly used in the sterilization, hygiene supervision, etc. in manufacture and synthetic process, and water-and-sewage institution of various chemicals and drugs, and foodstuffs, Or as a gaseous ozone sensor which has an effect prominent as an object for the surveillance monitors of the ozone layer in the atmosphere which is effective in protecting all the living things which live on the earth from harmful ultraviolet rays, the semiconductor gas sensor using the composite metal oxide which grows into this invention is the optimal.

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[Translation done.]

## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1]The composition diagram of a  $MgO$ - $ZnO$ - $In_2O_3$  system composite metal oxide (mol% display).

[Explanations of letters or numerals]

- A ... 80.0 $ZnO$  and 20.0 $In_2O_3$
- B ... 65.0 $MgO$  and 35.0 $In_2O_3$
- C ... 35.0 $MgO$  and 65.0 $In_2O_3$
- D ... 20.0 $ZnO$  and 80.0 $In_2O_3$
- E ... 75.0 $ZnO$  and 25.0 $In_2O_3$
- F ... 55.0 $MgO$  and 45.0 $In_2O_3$
- G ... 45.0 $MgO$  and 55.0 $In_2O_3$
- H ... 40.0 $ZnO$  and 60.0 $In_2O_3$
- 1 ... 50.0 $MgO$  and 50.0 $In_2O_3$
- 2 ... 66.7 $ZnO$  and 33.3 $In_2O_3$
- 3 ... 15.0 $MgO$ , 48.0 $ZnO$ , and 37.0 $In_2O_3$
- 4 ... 20.0 $MgO$ , 50.0 $ZnO$ , and 30.0 $In_2O_3$
- 5 ... 30.0 $MgO$ , 50.0 $ZnO$ , and 20.0 $In_2O_3$
- 6 ... 47.0 $MgO$ , 16.0 $ZnO$ , and 37.0 $In_2O_3$

[Drawing 2]The response characteristic over the gaseous chlorine of the composite metal oxide thin film sensor which has 2 $MgO$ , 6 $ZnO$ , and a 5 $In_2O_3$  presentation.

[Explanations of letters or numerals]

- 7 ... Concentration 50ppm 8 ... Concentration of 1.0 ppm
- 9 ... Concentration 0.5ppm 10 ... Concentration of 0.2 ppm

[Drawing 3]Gaseous chlorine concentration dependence of the sensitivity to the gaseous chlorine of the composite metal oxide thin film sensor which has 2 $MgO$ , 6 $ZnO$ , and a 5 $In_2O_3$  presentation.

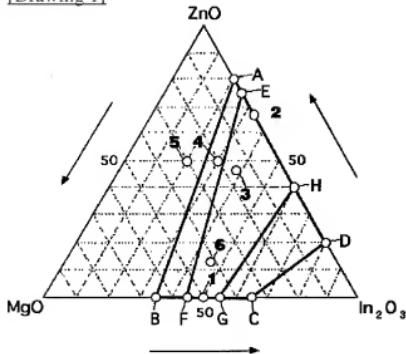
[Drawing 4]Gaseous ozone concentration dependence of the sensitivity to the gaseous ozone of the composite metal oxide thin film sensor which has 4 $MgO$ , 2 $ZnO$ , and a 5 $In_2O_3$  presentation.

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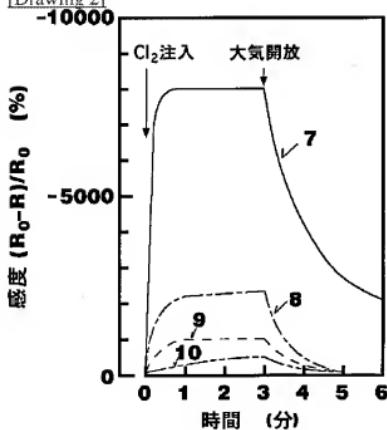
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## DRAWINGS

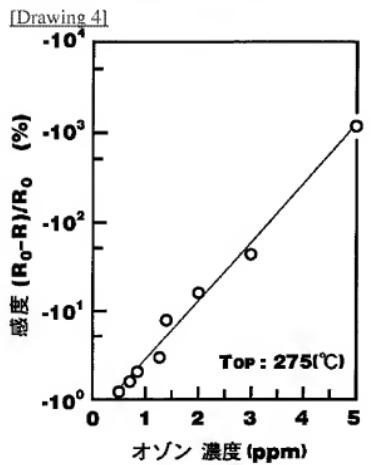
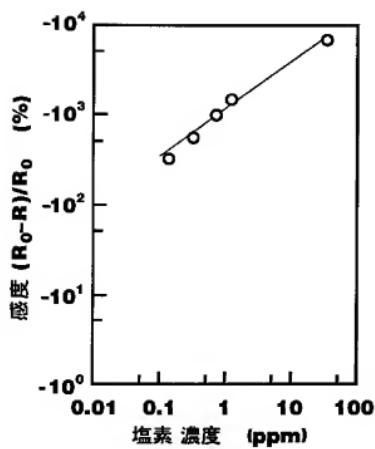
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]